

### Supporting Information for:

Correlation of Free Radical Copolymerization Behavior and Copolymer Properties with the Strength of  $\pi$ - $\pi$  Stacking Interactions between Aromatic Fluorocarbons and Aromatic Hydrocarbons: Copolymerization of Styrene and Fluorinated Styrenes at the Two Extreme Levels of Fluorination

by

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**Table S1.** Results of the Radical Copolymerizations of Styrene (St) and 2,3,4,5,6-Pentafluorostyrene (PFS).

Feed Composition: mol% St	Monomer Conversion <sup>a</sup> (%)		Copolymer Composition: mol% St		Copolymer Yield <sup>b</sup> (%)
	St	PFS	<sup>1</sup> H NMR	EA	
Bulk, 70 °C, benzoyl peroxide as initiator, 25 min					
90	5	6	88		2.3
80	1	10	82		1.6
70	3	2	76		8.9
70	8	8	59		10.4
60	2	2	62		8.4
50	10	10	57		6.0
50	<1	<1	50		12.0
40	8	9	46		8.5
30	10	8	44		8.0
30	<1	9	41		10.2
20	8	1	38		5.4
11	<1	<1	24		6.3
5	10	11	17		6.9
Bulk, 25 °C, <i>t</i> -butylperoxy pivalate as initiator, 2.5 h					
90	11	10	77		1.8
90	<1	15	75		
80	5	10	62		1.6
80	2	9	64		
70	5	6	57		1.2
60	10	7	50		<1
50	3	3	55		<1
40	8	5	45		1.5
30	2	10	40		1.2
30	9	9	43		<1
20	5	6	34		<1
18	<1	7	36		
10	6	2	23		1.6
10	6	5	24		<1
5	6	6	21		<1

25 °C, redox conditions, 2.5 h					
90	<1	<1	78	79	2.4
78	6	16	70	70	3.6
68	14	18	65	61	4
60	<1	<1	61	55	2.2
50	<1	<1	50	50	<1
50	<1	<1	49		<1
50	6	6	48		1.7
40	<1	<1	48		1.6
in toluene, 70 °C, benzoyl peroxide as initiator, 35 min					
90	<1	<1	84	82	2.8
90	10	3	84	82	3
80	20	<1	71	72	6.9
70	<1	28	65	66	7.8
68	<1	<1	64	64	8.3
59	7	10	58	57	10.8
50	19	19	54		-
48	13	11	54	52	12
40	<1	<1	50	46	5.7
31	<1	<1	43	41	6.7
30	<1	<1	42	40	8.4
20	28	2	35	33	2.8
11	5	1	23	21	7.6
10	6	6	24	20	3.5
in toluene, 25 °C, <i>t</i> -butylperoxy pivalate as initiator, 3 h					
90	<1	15	75		1.2
90	<1	<1	72		2
90	<1	<1	69		<1
80	2	9	64		<1
79	10	3	66		2.7
70	<1	5	69		<1
69	<1	<1	68		1.2
60	<1	<1	66	53	5
60	9	9	57		1.9
50	<1	<1	62	49	1.9
50	<1	<1	62	51	1.9
49	<1	<1	43		<1
31	<1	4	40		<1
30	7	<1	43	41	1.7
18	7	<1	36	30	1.6
12	11	5	29		2.9
11	2	4	23		21

<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopy using *n*-butyl acetate or diglyme (redox system) as internal standards.

<sup>b</sup> Determined gravimetrically after precipitating the copolymer.

**Table S2.** Results of the Radical Copolymerizations of Styrene (St) and 4-Fluorostyrene (4FS).

Feed Composition: mol% St	Monomer Conversion <sup>a</sup> (%)		Copolymer Composition: mol% St	Copolymer Yield <sup>b</sup> (%)
	St	4FS		
Bulk, 70 °C, benzoyl peroxide as initiator, 30 min				
90	12	7	90	3.6
90	8	<1	90	4.2
80	2	11	79	2.5
79	4	10	81	3.6
79	9	<1	83	<1
72	<1	7	66	2.9
71	3	10	72	4.1
69	<1	10	68	2.7
69	9	10	65	2.7
61	7	9	65	1.2
60	7	8	58	6.3
51	3	<1	50	5.4
51	7	<1	49	4.5
50	2	2	49	7.0
49	8	8	53	1.7
41	8	3	39	8.5
32	4	6	36	5.6
31	7	5	35	2.5
23	<1	<1	27	1.3
22	8	4	27	2.6
21	6	3	27	3.1
12	5	8	15	3.2
11	<1	<1	16	1.7
10	9	1	12	3.2
25 °C, redox conditions, 2.5 h				
90	6	2	91	1.2
90	18	6	90	1.6
80	5	<1	82	1.9
79	20	10	81	1.5
79	6	<1	83	2.4
70	1.3	<1	72	1.5
70	0	9	69	1.4
68	<1	<1	71	2.1
60	<1	<1	64	1.2
59	6	2	62	1.2
59	<1	<1	64	1.1
50	<1	<1	55	1.6
50	<1	<1	55	1.1
49	10	6	54	2.2
43	18	20	45	4.3

39	<1	<1	46	1.3
30	8	8	37	3.9
30	<1	<1	30	<1
29	<1	<1	34	<1
20	<1	<1	27	3.1
10	<1	4	15	1.8

<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopy using diglyme as an internal standard.

<sup>b</sup> Determined gravimetrically after precipitating the copolymer.

**Table S3.** Elemental Composition of Copolymers of Styrene (St) and 2,3,4,5,6-Pentafluorostyrene.<sup>a</sup>

Feed Composition: mol% St	Elemental Copolymer Composition		mol% St in Copolymer
	% C	% H	
Bulk, 25 °C, redox conditions, 2.5 h			
50	64.443	3.580	50
60	66.535	3.773	55
68	68.870	4.247	61
78	73.030	4.852	70
90	77.841	5.602	79
in toluene, 70 °C, benzoyl peroxide as initiator, 35 min			
90	79.859	5.678	82
90	80.098	5.795	82
80	74.418	4.852	72
70	71.369	4.531	66
68	70.186	4.318	64
59	67.207	3.751	57
48	65.071	3.480	52
40	63.061	3.248	46
31	61.177	3.031	41
30	60.888	3.047	40
20	58.482	2.687	33
11	54.798	2.190	21
10	54.606	2.103	20
in toluene, 25 °C, <i>t</i> -butylperoxy pivalate, 3 h			
18	57.410	2.601	30
30	61.157	3.072	41
50	64.076	3.525	49
49	64.964	3.538	51
60	65.795	3.852	53

<sup>a</sup> Copolymer composition determined from mean of %C from two replications after removing unreacted monomers by precipitating the copolymer

**Table S4.** Data Used to Determine the Reactivity Ratios of Styrene (St, M<sub>1</sub>) and 2,3,4,5,6-Pentafluorostyrene (M<sub>2</sub>) in their Radical Copolymerizations.

Feed Composition: mol% St	mol% St in Copolymer <sup>a</sup>	Fineman-Ross Parameters <sup>b</sup>		Kelen-Tüdös Parameters <sup>c</sup>	
		$F = x^2/y$	$G = [x(y-1)]/y$	$\zeta = F/(\alpha+F)$	$\eta = G/(\alpha+F)$
Bulk, 70 °C, benzoyl peroxide as initiator, 25 min, $\alpha = 0.386$					
90	88	11.0	7.77	0.966	0.679
80	82	3.51	3.12	0.901	0.801
70	76	1.71	1.60	0.816	0.763
70	59	3.77	0.712	0.907	0.171
60	62	1.38	0.580	0.781	0.328
50	57	0.750	0.248	0.660	0.218
50	50	1.00	0.00	0.722	0.000
40	46	0.522	-0.116	0.575	-0.128
30	44	0.234	-0.117	0.379	-0.189
30	41	0.265	-0.188	0.407	-0.289
20	38	0.102	-0.158	0.209	-0.324
11	24	0.0487	-0.268	0.112	-0.617
5	17	0.0135	-0.204	0.0338	-0.511
Bulk, 25 °C, <i>t</i> -butylperoxy pivalate as initiator, 2.5 h, $\alpha = 0.530$					
90	77	24.2	6.31	0.979	0.255
90	75	27.0	6.00	0.981	0.218
80	62	9.82	1.55	0.949	0.150
80	64	8.99	1.75	0.944	0.184
70	57	4.08	0.578	0.885	0.125
60	50	2.25	0.00	0.809	0.00
50	55	0.820	0.180	0.607	0.133
40	45	0.544	-0.222	0.507	-0.207
30	40	0.276	-0.214	0.342	-0.266
30	43	0.244	-0.140	0.315	-0.181
20	34	0.121	-0.235	0.186	-0.361
18	36	0.0861	-0.171	0.140	-0.278
10	23	0.0412	-0.260	0.0721	-0.455
5	17	0.0104	-0.145	0.0192	-0.268
25 °C, redox conditions, 2.5 h, $\alpha = 3.32$					
90	78	22.8	6.46	0.873	0.247
90	79 <sup>d</sup>	21.5	6.61	0.867	0.266
78	70	5.41	2.03	0.620	0.233
78	70 <sup>d</sup>	5.41	2.03	0.620	0.233
68	65	2.43	0.983	0.423	0.171
68	61 <sup>d</sup>	2.89	0.763	0.466	0.123
60	61	1.44	0.538	0.303	0.113
60	55 <sup>d</sup>	1.84	0.270	0.357	0.0524
50	50	1.00	0.00	0.232	0.00

50	50 <sup>d</sup>	1.00	0.00	0.232	0.00
50	49	1.04	-0.0406	0.239	-0.00932
50	48	1.18	-0.0869	0.262	-0.0193
40	48	0.482	-0.0556	0.127	-0.0146
in toluene, 70 °C, benzoyl peroxide as initiator, 35 min, $\alpha = 0.832$					
90	84	15.4	7.29	0.949	0.448
90	82 <sup>d</sup>	17.8	7.03	0.955	0.378
90	84	15.4	7.29	0.949	0.448
90	82 <sup>d</sup>	17.8	7.03	0.955	0.378
80	71	6.64	2.34	0.889	0.313
80	72 <sup>d</sup>	6.23	2.44	0.882	0.346
70	65	2.92	1.08	0.778	0.288
70	66 <sup>d</sup>	2.80	1.13	0.771	0.311
68	65	2.43	0.983	0.745	0.301
68	64 <sup>d</sup>	2.54	0.931	0.753	0.276
59	58	1.50	0.396	0.643	0.170
59	57 <sup>d</sup>	1.56	0.357	0.652	0.149
50	54	0.855	0.145	0.507	0.0860
48	54	0.728	0.134	0.467	0.0859
48	52 <sup>d</sup>	0.784	0.0684	0.485	0.0423
40	50	0.445	0.00	0.348	0.00
40	46 <sup>d</sup>	0.522	-0.116	0.386	-0.0857
31	43	0.267	-0.146	0.243	-0.133
31	41 <sup>d</sup>	0.290	-0.197	0.258	-0.176
30	42	0.254	-0.164	0.234	-0.151
30	40 <sup>d</sup>	0.276	-0.143	0.249	-0.129
20	35	0.116	-0.215	0.122	-0.227
20	33 <sup>d</sup>	0.127	-0.258	0.132	-0.269
11	23	0.0514	-0.291	0.0582	-0.329
11	21 <sup>d</sup>	0.0578	-0.342	0.0650	-0.384
10	24	0.0390	-0.241	0.0448	-0.277
10	20 <sup>d</sup>	0.0493	-0.333	0.0559	-0.378
in toluene, 25 °C, <i>t</i> -butylperoxy pivalate as initiator, 3 h, $\alpha = 1.28$					
90	75	27.0	6.00	0.955	0.212
90	72	31.5	5.50	0.961	0.168
90	69	36.3	4.96	0.966	0.132
80	64	8.99	1.75	0.875	0.170
79	66	7.30	1.82	0.851	0.212
70	69	2.43	1.29	0.654	0.347
69	68	2.35	1.18	0.647	0.325
60	66	1.16	0.727	0.475	0.298
60	53 <sup>d</sup>	1.99	0.173	0.608	0.0529
60	57	1.69	0.372	0.568	0.125
50	49	1.04	-0.0406	0.448	-0.0175
50	62 <sup>d</sup>	0.613	0.387	0.323	0.204
49	62	0.567	0.371	0.306	0.201

49	51 <sup>d</sup>	0.888	0.0370	0.409	0.0170
49	43	1.22	-0.314	0.487	-0.125
31	40	0.302	-0.224	0.191	-0.141
30	43	0.244	-0.140	0.160	-0.0917
30	41 <sup>d</sup>	0.265	-0.188	0.171	-0.121
18	36	0.0861	-0.171	0.0629	-0.125
18	30 <sup>d</sup>	0.113	-0.293	0.0809	-0.210
12	29	0.0453	-0.197	0.0341	-0.148
11	23	0.0514	-0.291	0.0385	-0.218

<sup>a</sup> Unless noted otherwise, copolymer composition determined by <sup>1</sup>H NMR analysis of the copolymer after removing unreacted monomers by precipitating the copolymer.

<sup>b</sup>  $x = [M_1]/[M_2]$  and  $y = d[M_1]/d[M_2]$ .

<sup>c</sup>  $\alpha = (F_H F_L)^{1/2}$ , and  $F_H$  and  $F_L$  are the highest and lowest values of  $F$ , respectively.

<sup>d</sup> Copolymer composition determined by elemental analysis.

**Table S5.** Data Used to Determine the Reactivity Ratios of Styrene (St,  $M_1$ ) and 4-Fluorostyrene ( $M_2$ ) in their Radical Copolymerizations.

Feed Composition: mol% St	mol% St in Copolymer <sup>a</sup>	Fineman-Ross Parameters <sup>b</sup>		Kelen-Tüdös Parameters <sup>c</sup>	
		$F = x^2/y$	$G = [x(y-1)]/y$	$\eta = G/(\alpha+F)$	$\zeta = F/(\alpha+F)$
Bulk, 70 °C, benzoyl peroxide as initiator, 30 min, $\alpha = 0.853$					
90	90	9.00	8.00	0.812	0.913
90	90	9.00	8.00	0.812	0.913
80	79	4.26	2.94	0.575	0.833
79	81	3.32	2.88	0.690	0.796
79	83	2.90	2.99	0.797	0.773
72	66	3.40	1.25	0.294	0.799
71	72	2.34	1.50	0.470	0.733
69	68	2.34	1.18	0.370	0.733
69	65	2.92	1.08	0.286	0.774
61	65	1.31	0.721	0.333	0.606
60	58	1.63	0.413	0.166	0.656
51	50	1.08	0.00	0.000	0.559
51	49	1.13	-0.0422	-0.0213	0.570
50	49	1.04	-0.0406	-0.0214	0.549
49	53	0.817	0.111	0.0665	0.489
41	39	0.756	-0.393	-0.244	0.470
32	36	0.394	-0.366	-0.294	0.316
31	35	0.375	-0.386	-0.314	0.305
23	27	0.242	-0.509	-0.465	0.221
22	27	0.215	-0.480	-0.449	0.201
21	27	0.191	-0.453	-0.434	0.183
12	15	0.105	-0.637	-0.665	0.110
11	16	0.0809	-0.529	-0.566	0.0866
10	12	0.0906	-0.705	-0.747	0.0960

25 °C, redox conditions, 2.5 h, $\alpha = 0.794$					
90	91	8.01	8.11	0.921	0.910
90	90	9.00	8.00	0.817	0.919
80	82	3.51	3.12	0.725	0.816
79	81	3.32	2.88	0.700	0.807
79	83	2.90	2.99	0.809	0.785
70	72	2.11	1.42	0.489	0.727
70	69	2.43	1.29	0.400	0.754
68	71	1.83	1.26	0.480	0.697
60	64	1.26	0.657	0.320	0.613
59	62	1.27	0.557	0.270	0.615
59	64	1.16	0.631	0.323	0.594
50	55	0.820	0.180	0.112	0.508
50	55	0.820	0.180	0.112	0.508
49	54	0.789	0.140	0.0884	0.498
43	45	0.695	-0.168	-0.113	0.467
39	46	0.479	-0.111	-0.0872	0.376
30	30	0.429	-0.571	-0.467	0.351
30	37	0.314	-0.301	-0.272	0.283
29	34	0.323	-0.384	-0.344	0.289
20	27	0.169	-0.426	-0.442	0.176
10	15	0.0700	-0.520	-0.602	0.0810

<sup>a</sup> Copolymer composition determined by <sup>1</sup>H NMR analysis of the copolymer after removing unreacted monomers by precipitating the copolymer.

<sup>b</sup>  $x = [M_1]/[M_2]$  and  $y = d[M_1]/d[M_2]$ .

<sup>c</sup>  $\alpha = (F_H F_L)^{1/2}$ ; and  $F_H$  and  $F_L$  are the highest and lowest values of  $F$ , respectively.

**Table S6.** Comonomer Reactivity Ratios ( $r_{St}$ ,  $r_{FS}$ ) and Their Products Determined by the Kelen-Tüdös Method in the Radical Copolymerizations of Styrene (St) with 2,3,4,5,6-Pentafluorostyrene (PFS) and 4-Fluorostyrene (4FS).

Conditions	Reactivity Ratios		
	$r_{St}$	$r_{FS}$	$r_{St}r_{FS}$
<b>St-PFS</b>			
70 °C, bulk	0.64	0.27	0.17
70 °C, toluene	0.46	0.30	0.14
60 °C, bulk <sup>a</sup>	0.43	0.22	0.095
25 °C, bulk	0.21	0.22	0.046
25 °C, redox	0.35	0.26	0.091
25 °C, toluene	0.28	0.17	0.048
<b>St-4FS</b>			
70 °C, bulk	0.86	0.72	0.62
25 °C, redox	1.0	0.68	0.68

<sup>a</sup> From reference 39 using azobisisobutyronitrile as the initiator and the Fineman-Ross method of calculation.



**Table S7.** Glass Transition Temperatures ( $T_g$ ) of Blends of Polystyrene (PSt) and Poly(4-fluorostyrene) (P4FS).<sup>a</sup>

Mol% PSt in Blend <sup>b</sup>	$T_{g1}$ (°C)	$T_{g2}$ (°C)	Isolated Yield <sup>c</sup> (%)
100	102.0		-
87	103.4	113.2	90
76	102.7	111.2	89
69	102.6	112.0	86
66	102.7	111.0	94
55	102.4	110.5	95
39	103.2	111.2	91
34	102.6	110.9	86
21	102.8	110.6	86
12	104.0	111.6	81
0	111.1		-

<sup>a</sup>  $T_g$  determined by differential scanning calorimetry as mean of values from second and third heating scans at 10 °C/min; PSt  $M_n = 3.53 \times 10^4$ ,  $pdi = 1.85$ ; P4FS  $M_n = 8.63 \times 10^4$ ,  $pdi = 2.86$ .

<sup>b</sup> Determined by <sup>1</sup>H NMR analysis after precipitating the blends.

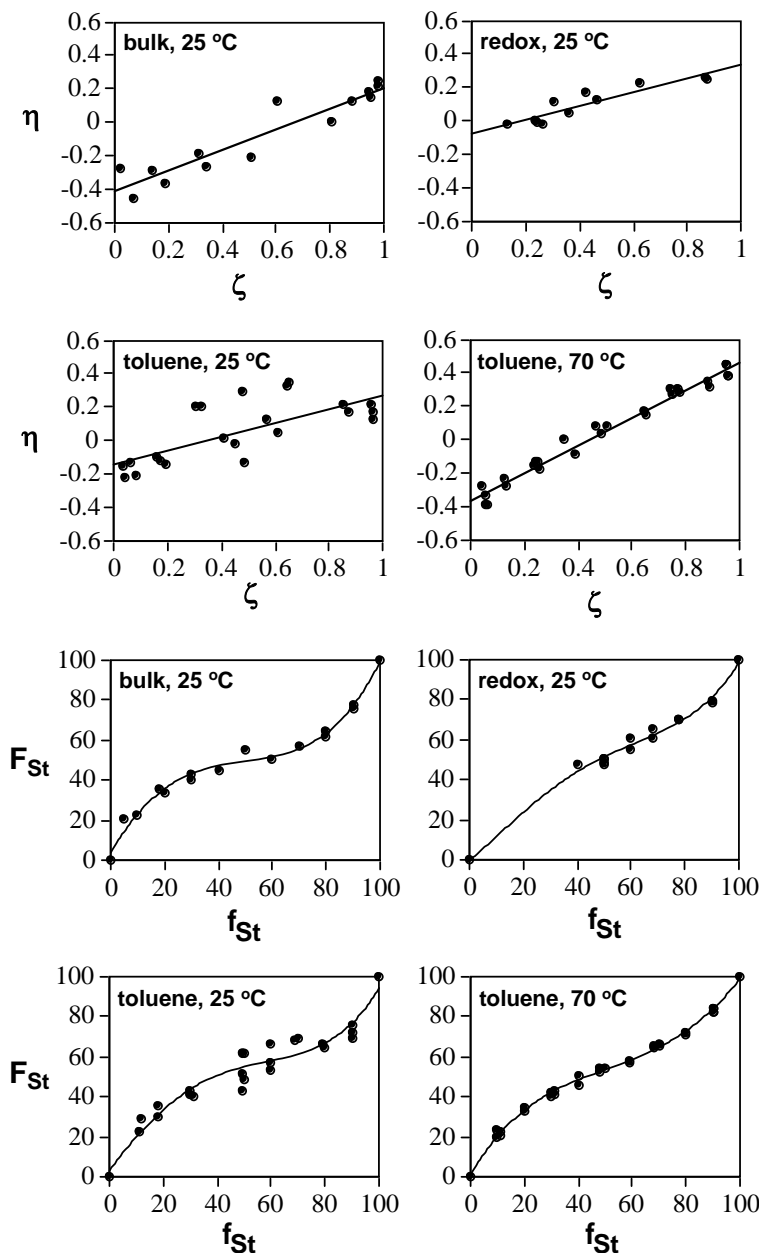
<sup>c</sup> Determined gravimetrically after precipitating the blends.

**Table S8.** Contact Angles of Poly(styrene-*co*-2,3,4,5,6-pentafluorostyrene) (St-PFS) and Poly(styrene-*co*-4-fluorostyrene) (St-4FS) Films Cast from Toluene.<sup>a</sup>

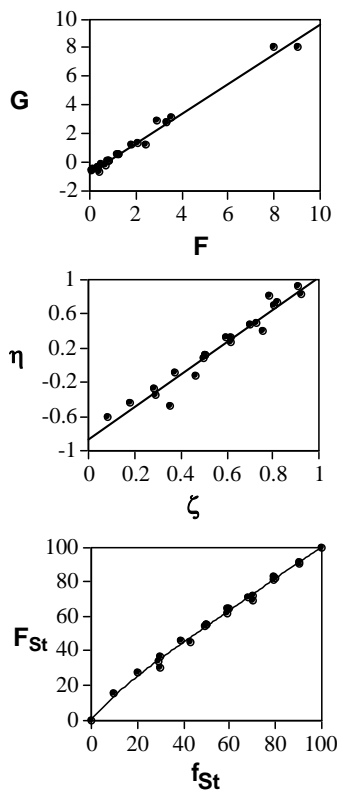
mol% St in copolymer <sup>b</sup>	Contact Angle ( $\theta_c$ )	
	Water	Ethylene Glycol
St-PFS		
100	90.0 ± 0.0	62.2 ± 0.2
78	92.5 ± 0.5	65.5 ± 0.5
76	94.2 ± 0.4	65.8 ± 1.3
57	94.8 ± 0.4	70.2 ± 1.3
50	96.0 ± 0.0	70.0 ± 0.7
44	95.5 ± 0.5	71.8 ± 0.4
24	97.0 ± 0.7	74.8 ± 0.4
0	100.0 ± 0.0	82.0 ± 1.0
St-4FS		
88	91.2 ± 0.4	
53	93.2 ± 0.8	
27	95.0 ± 0.0	
0	96.0 ± 1.2	

<sup>a</sup> Mean and standard deviation of four contact angle measurements; copolymers produced by radical copolymerization of St with PFS or 4FS in bulk at 70 °C using benzoyl peroxide as the initiator.

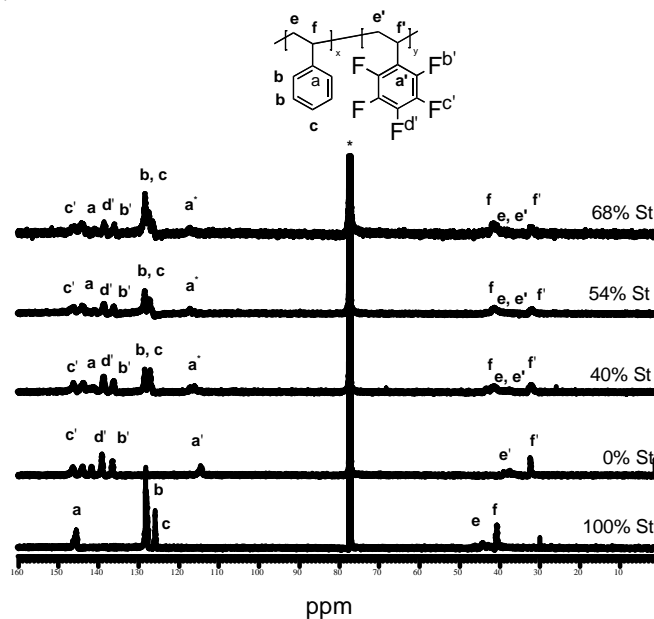
<sup>b</sup> Copolymer composition determined by <sup>1</sup>H NMR analysis of the copolymer after removing unreacted monomers by precipitating the copolymer.



**Figure S1.** Kelen-Tüdös (KT:  $\eta$  vs.  $\zeta$ ) and Mayo-Lewis ( $F_{St}$  vs.  $f_{St}$ ) plots used to determine the reactivity ratios in the radical copolymerizations of styrene ( $M_1$ ) and 2,3,4,5,6-pentafluorostyrene ( $M_2$ ) in bulk at room temperature for 2.5 h using *t*-butylperoxy pivalate as the initiator (KT:  $y = 0.618x - 0.410$ ); in bulk at room temperature for 2.5 h using redox conditions (KT:  $y = 0.426x - 0.077$ ); in toluene at room temperature for 3 h using *t*-butylperoxy pivalate as the initiator (KT:  $y = 0.410x - 0.134$ ); and in toluene at 70 °C for 35 min using benzoyl peroxide as the initiator (KT:  $y = 0.822x - 0.358$ ).



**Figure S2.** Fineman-Ross (top;  $y = 1.02x - 0.638$ ), and Kelen-Tüdös (middle;  $y = 1.89x - 0.856$ ) and Mayo-Lewis (bottom) plots used to determine the reactivity ratios in the radical copolymerization (2.5 h) of styrene ( $M_1$ ) and 4-fluorostyrene ( $M_2$ ) in bulk at room temperature using redox conditions.



**Figure S3.**  $^{13}\text{C}$  NMR spectra of polystyrene (PSt), poly(2,3,4,5,6-pentafluorostyrene) (PPFS), and P(St-co-PFS) with 40 mol% St, 54 mol% St, and 68 mol% St synthesized by radical (co)polymerization of 2,3,4,5,6-pentafluorostyrene and/or styrene in bulk at 70 °C for 25 min using 1 mol% benzoyl peroxide as the initiator; \* =  $\text{CDCl}_3$ .